

Definitions of VOC and ROG

Last Revised August 2000

1. U.S. EPA Definition of VOC (Volatile Organic Compounds):

The U.S. Environmental Protection Agency (U.S. EPA) defines and uses the term Volatile Organic Compounds (VOC). The term VOC is defined in the Federal Register. The original definition of VOC made reference to the vapor pressure of the compounds (greater than 0.1 millimeter of mercury) as a determinant of volatility. However, the current definition relies solely on a list of exempted compounds having "negligible photochemical reactivity".

U.S. EPA periodically exempts additional compounds. Proposed exemptions are pending. A summary follows.

RECENT FINAL RULEMAKINGS:

- (1) Acetone was exempted by final rule published June 16, 1995 (60 FR 31633).
- (2) Perchloroethylene was exempted by final rule published February 7, 1996 (61 FR 4588).
- (3) In response to petitions, the U.S. EPA exempted HFC 43-10mee, HCFC 225ca, and HCFC 225cb. The final rule was published October 8, 1996 (61 FR 52848), and became effective November 7, 1996.
- (4) The Alliance for Responsible Atmospheric Policy, Arlington, Virginia, petitioned to exempt 22 compounds, primarily HFCs and HCFCs, but later withdrew five of these. U.S. EPA exempted 16 of the 17 requested compounds (excluding HCFC-150a). The final rule was published August 25, 1997 (62 FR 44900), effective September 24, 1997.
- (5) U.S. EPA exempted Methyl acetate, in response to petition from Eastman Chemical, April 9, 1998 (63 FR 17331), effective May 11, 1998.

PENDING RULEMAKINGS AND PETITIONS (as of August 2000):

- (6) U.S. EPA published a proposal regarding possible exemption of tertiary-butyl acetate (t-butyl acetate) (64 FR 52731, September 30, 1999), in response to a petition from Lyondell Chemical Company. U.S. EPA is considering comments received to the proposal.
- (7) U.S. EPA, OAQPS, is rethinking aspects of its reactivity policy, such as a molar vs. gram basis for reactivity. A national workshop took place May 12-14, 1998 in North Carolina, and a Reactivity Research Working Group was formed to foster a public/private partnership to sponsor and guide scientific research regarding ozone reactivity.
- (8) U.S. EPA received petitions, which are pending review, requesting to exempt the following additional compounds:
 - Chlorobromomethane - from ICF Kaiser (SAI Division), San Rafael, California (11/95);
 - 1-Bromopropane - from EnviroTech International, Alameda, California (5/96);
 - Methyl bromide - from Chemical Manufacturers Association, Washington, D.C. (7/96);
 - N-Alkanes (C₁₂ - C₁₈) - from The Aluminum Association, Washington, D.C. (11/96);
 - Technical white oils - from The Printing Industries of America and Pennzoil Products Company (12/96);
 - Benzotrifluoride - from Occidental Chemical Company, Niagara Falls, NY (3/97);
 - Carbonyl sulfide (COS) - from E.I. du Pont de Nemours and Company (8/97).
 - trans-1,2-Dichloroethylene - from 3M Corporation, St. Paul, MN (10/97).
 - Dimethyl succinate and Dimethyl glutarate - from the Dibasic Esters Group, affiliated with the Synthetic Organic Chemical Manufacturers Association, Inc. (10/97);
 - Carbon disulfide - Texas Mid-Continent Oil and Gas Association (12/97);
 - Acetonitrile - BP Chemicals and GNI Chemicals Corporation (12/98);
 - Toluene diisocyanate (TDI) - Chemical Manufacturers Association (1/98);
 - HFC-227ea (1,1,1,2,3,3,3-Heptafluoropropane) - Great Lakes Chemical Corporation (2/98);
 - Methylene diphenyl diisocyanate (MDI) - Chemical Manufacturers Association (8/98);
 - 1,1,1,2,2,3,3-Heptafluoro-3-methoxy-propane (n-C3F7OCH3) - 3M Corporation;
 - Propylene Carbonate - Huntsman Corporation.

The complete federal definition and the list of exempted compounds to date are shown on the following page.

U.S. EPA Definition of VOC (as of August 2000): (based on final rules to date)

40 CFR Part 51 Section 51.100 Definitions.

- (s) **Volatile organic compounds (VOC)** means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

- (1) This includes any such organic compound other than the following, which have been determined to have negligible photochemical reactivity:

methane;	[74-82-8]*
ethane;	[74-84-0]
methylene chloride (dichloromethane);	[75-09-2]
1,1,1-trichloroethane (methyl chloroform);	[71-55-6]
1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113);	[76-13-1]
trichlorofluoromethane (CFC-11);	[75-69-4]
dichlorodifluoromethane (CFC-12);	[75-71-8]
chlorodifluoromethane (HCFC-22);	[75-45-6]
trifluoromethane (HFC-23);	[75-46-7]
1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114);	[76-14-2]
chloropentafluoroethane (CFC-115);	[76-15-3]
1,1,1-trifluoro-2,2-dichloroethane (HCFC-123);	[306-83-2]
1,1,1,2-tetrafluoroethane (HFC-134a);	[811-97-2]
1,1-dichloro-1-fluoroethane (HCFC-141b);	[1717-00-6]
1-chloro-1,1-difluoroethane (HCFC-142b);	[75-68-3]
2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124);	[2837-89-0]
pentafluoroethane (HFC-125);	[354-33-6]
1,1,2,2-tetrafluoroethane (HFC-134);	[359-35-3]
1,1,1-trifluoroethane (HFC-143a);	[420-46-2]
1,1-difluoroethane (HFC-152a);	[75-37-6]
parachlorobenzotrifluoride (PCBTF);	[98-56-6]
cyclic, branched, or linear completely methylated siloxanes;	[various]
acetone;	[67-64-1]
perchloroethylene (tetrachloroethylene);	[127-18-4]
3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca);	[422-56-0]
1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb);	[507-55-1]
1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee);	[138495-42-8]
difluoromethane (HFC-32);	[75-10-5]
ethylfluoride (HFC-161);	[353-36-6]
1,1,1,3,3,3-hexafluoropropane (HFC-236fa);	[690-39-1]
1,1,2,2,3-pentafluoropropane (HFC-245ca);	[679-86-7]
1,1,2,3,3-pentafluoropropane (HFC-245ea);	[24270-66-4]
1,1,1,2,3-pentafluoropropane (HFC-245eb);	[431-31-2]
1,1,1,3,3-pentafluoropropane (HFC-245fa);	[460-73-1]
1,1,1,2,3,3-hexafluoropropane (HFC-236ea);	[431-63-0]
1,1,1,3,3-pentafluorobutane (HFC-365mfc);	[406-58-6]
chlorofluoromethane (HCFC-31);	[593-70-4]
1-chloro-1-fluoroethane (HCFC-151a);	[1615-75-4]
1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a);	[354-23-4]
1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane (C ₄ F ₉ OCH ₃);	[163702-07-6]
2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF ₃) ₂ CF ₂ OC ₂ H ₅);	[163702-08-7]
1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (C ₄ F ₉ OC ₂ H ₅);	[163702-05-4]
2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF ₃) ₂ CF ₂ OC ₂ H ₅);	[163702-06-5]
methyl acetate	[79-20-9]
and perfluorocarbon compounds which fall into these classes:	[various]
(I) Cyclic, branched, or linear, completely fluorinated alkanes;	
(ii) Cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;	
(iii) Cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and	
(iv) Sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.	

* NOTE: Chemical Abstract Service (CAS) identification numbers have been included in brackets [] for convenience.

2. California Air Resources Board's Definition of ROG (Reactive Organic Gases):

The California Air Resources Board's (ARB's) Emission Inventory Branch (EIB) uses the terms Total Organic Gases (TOG) and Reactive Organic Gases (ROG). California air pollution control districts report Total Organic Gases (TOG) to the Air Resources Board's emission inventory.

For each source category, the ARB derives a value for the Reactive Organic Gases (ROG) by multiplying the reported TOG by the Fraction of Reactive Organic Gases (FROG). Each source category is keyed to one of several hundred available chemical speciation profiles. For each category, the FROG value is calculated as the weight fraction of those species designated by the ARB as reactive in the speciation profile applicable to the category. The ARB's organic gas speciation profiles are available for download from the ARB's web site at www.arb.ca.gov.

The relationships among these organic gas terms are summarized as follows:

$$\begin{array}{ccccc} \text{TOG} & - & \text{Exempt cmpds} & = & \text{ROG} \\ \text{(Total Organic Gas)} & & \text{[ARB list of methane,} & & \text{(Reactive Organic Gas)} \\ & & \text{CFCs, etc.]} & & \end{array}$$

$$\begin{array}{ccccc} \text{TOG} & \times & \text{FROG} & = & \text{ROG} \\ \text{(Total Organic Gas)} & & \text{(Fraction of Reactive} & & \text{(Reactive Organic Gas)} \\ & & \text{Organic Gas)} & & \end{array}$$

Background Regarding Federal vs. State Exempt List: The original "Air Pollution Emission Inventory Program" manual, ARB, March 1982, listed the compounds which the ARB initially treated as exempted from ROG. The list differed somewhat from the U.S. EPA's list of exempted VOCs even at the time, in that ARB's definition of ROG did not exempt Ethane. As discussed in the prior section, U.S. EPA later exempted additional compounds from the federal definition of VOC as well.

Subsequently, the Air Resources Board was petitioned regarding exemptions from the ARB's regulations. The ARB staff formed a Reactive Organic Gas Technical Committee (ROGTC), made up of staff from the ARB's affected divisions and district representatives, to systematically evaluate the proposed exemption of these compounds. At a public hearing in September 1995, the Air Resources Board took action to revise the definition of "Volatile Organic Compounds" that is used in the consumer products regulations, based on the recommendations of the ROGTC. Methyl siloxanes were added to the list of exempted compounds, and parachlorobenzotrifluoride, acetone, and ethane were added to the list of exempted compounds with the qualifier that they are "low-reactive organic compounds which have been exempted by the U.S. EPA". Based on the ROGTC's analysis, the staff similarly modified the overall inventory definition of ROG to extend the Board's action on the consumer products regulation "VOC" definition to "ROG" for all inventory applications.

The Air Resources Board exempted Perchloroethylene from the definition of VOC in the consumer products regulations in November 1996. In response to industry petition, the Air Resources Board approved the exemption of Methyl acetate from the definition of VOC in the ARB's regulations for aerosol coatings, consumer products, and antiperspirants and deodorants at a public hearing on November 19, 1998.

As noted above, the ARB's list of compounds has two parts, including a second group of low-reactive organic compounds which have been exempted by the U.S. EPA®. This designation is used for compounds that are expected to have low, but not insignificant, ozone formation impacts in the near-term; however, their future new uses and emissions need to be tracked, and the exemption revisited, if necessary, to ensure there is no future degradation of air quality resulting from increased usage.

Likewise, some compounds that have been exempted from the definition of ROG or VOC may have other adverse impacts, such as toxicity, stratospheric ozone depletion potential, or greenhouse gas potential, that must be considered. Therefore, "exemption" from the definition of ROG or VOC is not an automatic endorsement for increased usage of a compound.

The complete definitions and the list of exempted compounds to date are shown on the following page

ARB's Definitions of TOG and ROG (as of August 2000):

Total Organic Gases (TOG) means compounds of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate.

Reactive Organic Gases (ROG) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, and excluding the following:

	<u>CAS</u> *	<u>(TAC)</u> **
(1)		
methane;	[74-82-8]	
methylene chloride (dichloromethane);	[75-09-2]	TAC
1,1,1-trichloroethane (methyl chloroform);	[71-55-6]	TAC
trichlorofluoromethane (CFC-11);	[75-69-4]	
dichlorodifluoromethane (CFC-12); [75-71-8]		
1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113);	[76-13-1]	
1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114);	[76-14-2]	
chloropentafluoroethane (CFC-115);	[76-15-3]	
chlorodifluoromethane (HCFC-22);	[75-45-6]	
1,1,1-trifluoro-2,2-dichloroethane (HCFC-123);	[306-83-2]	
2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124);	[2837-89-0]	
1,1-dichloro-1-fluoroethane (HCFC-141b);	[1717-00-6]	
1-chloro-1,1-difluoroethane (HCFC-142b);	[75-68-3]	
trifluoromethane (HFC-23);	[75-46-7]	
pentafluoroethane (HFC-125);	[354-33-6]	
1,1,2,2-tetrafluoroethane (HFC-134); [359-35-3]		
1,1,1,2-tetrafluoroethane (HFC-134a);	[811-97-2]	
1,1,1-trifluoroethane (HFC-143a);	[420-46-2]	
1,1-difluoroethane (HFC-152a);	[75-37-6]	
cyclic, branched, or linear completely methylated siloxanes;	[various]	
the following classes of perfluorocarbons:	[various]	
(A) cyclic, branched, or linear, completely fluorinated alkanes;		
(B) cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;		
(C) cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and		
(D) sulfur-containing perfluorocarbons with no unsaturations and with the sulfur bonds only to carbon and fluorine; and		
(2) the following low-reactive organic compounds which have been exempted by the U.S. EPA:		
acetone;	[67-64-1]	
ethane;	[74-84-0]	
methyl acetate;	[79-20-9]	
perchloroethylene; and	[127-18-4]	TAC
parachlorobenzotrifluoride (1-chloro-4-trifluoromethyl benzene).	[98-56-6]	

* NOTE: Chemical Abstract Service (CAS) identification numbers have been included in brackets [] for convenience.

** NOTE: "TAC" indicates compounds that have been identified by the ARB as Toxic Air Contaminants (TAC). Their "exemption" from the definition of ROG or VOC is not an endorsement for their increased usage.

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